

ALKALI AND ALKALINE EARTH PROMOTED CATALYSTS FOR COAL LIQUEFACTION APPLICATIONS

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INTRODUCTION

The promotion of Co (or Ni) Mo/Alumina hydrotreating catalysts with percentage quantities of alkali and alkaline earth metals has been proposed as a means of reducing carbon formation when the catalyst is subjected to a high coking environment (1, 2, 3). We recently reported the results of a study in which a sodium promoted NiMo catalyst was compared with the untreated catalyst while hydrotreating a coal-derived liquid (4). In terms of hydrogenation activity, the treated and untreated catalysts were essentially equivalent. Both possessed excellent activity and this activity was well maintained over the 400 hour run duration. Carbon deposition on the used catalyst was substantially reduced by the sodium treatment. The incorporation of sodium into the catalyst did, however, reduce the hydrodenitrogenation activity. The present study was undertaken to ascertain whether similar effects could be realized by promotion with the alkaline earth metals.

EXPERIMENTAL

Catalyst deactivation runs were conducted in the bench scale trickle bed hydro-treater described previously (4). The reactor is charged with only three grams of catalyst, and at this scale of operation it is difficult to obtain reliable kinetics information due principally to the low liquid mass velocities characteristic of such systems (5). One should therefore not attach too much significance to the absolute values of the reported rate constants. Rather it is the relative values of the rate constants that is significant. The system has proven to be a reliable catalyst screening tool as the data are reproducible and conditions are chosen such that differences in activity level are readily observed.

The catalyst selected for this investigation is a CoMo/Alumina catalyst (Amocat 1A-nominal 16 wt% MoO₃, 3 wt% CoO) provided by the Amoco Oil Company. This catalyst was designed specifically for coal liquefaction applications as described in (6, 7). A calcium promoted catalyst was prepared from the Amocat 1A by the incipient wetness impregnation with aqueous calcium nitrate followed by calcining for four hours at 450°C. The finished catalyst contained 5.3 wt% CaO. A magnesium promoted catalyst (3.8 wt% MgO) was prepared similarly. Both weight percentages correspond to a loading of 0.9 mole alkaline earth per mole molybdenum. Properties of all three catalysts are summarized in Table I. The catalysts were sulfided in 10% H₂S/H₂ prior to characterization.

The feedstock employed in this investigation is a mildly hydrogenated creosote oil (560-835°F) spiked with 20 wt% ash free coal liquid vacuum bottoms (1000°F) obtained from the Advanced Coal Liquefaction Research Facility at Wilsonville, Alabama, Run 247. Properties of the feedstock HCO1-R are compiled in Table II.

Crude kinetics models were developed for the HC01-R/Amocat 1A feedstock/catalyst system in a manner similar to the procedure described by Baker, et al. (4). Details are provided in a final DOE report (8). The hydrogen uptake kinetics are first order reversible; whereas, the hydrodenitrogenation kinetics are taken to be first order and irreversible. Deactivation run conditions are summarized in Table III. These conditions, while severe by hydrotreating standards, are not out of line when compared to coal liquefaction conditions.

BET surface areas were calculated from the nitrogen adsorption isotherm at liquid nitrogen temperatures. Pore size distributions were obtained by mercury porosimetry. Prior to characterization, all used catalysts were extracted in tetrahydrofuran (THF) for 24 hours and dried under vacuum at 100°C for 48 hours. The used THF extracted catalysts were analyzed for carbon-hydrogen content in a combustion tube apparatus. All catalysts were subjected to acid sites characterization by the Temperature Programmed Desorption (TPD) of t-butylamine (9, 10). We calculate a Relative Acid Density (RAD) by dividing the high temperature "β-peak" area by the BET surface area. This quantity is an indication of the acid sites density when compared with other catalysts in the program. Attempts to interpret the maximum peak temperature as a measure of acid site strength are complicated by the decomposition of the adsorbed base prior to its desorption from the sample (11).

RESULTS AND DISCUSSION

Hydrogen uptake deactivation curves for the three catalysts are plotted in Figure 1. While there may have been some loss in day one activity due to the addition of promotor metals, it seems clear that the hydrogenation activities are essentially equivalent after the first few hours on stream. Similar results were observed in an earlier study of sodium promoted catalysts (4). In contrast the hydrodenitrogenation activities are significantly lowered by the incorporation of alkaline earth metals into the catalyst, Figure 2. (An upset was experienced prior to the last balance period during the run with unpromoted catalyst, hence the dashed line.) Furthermore, the reduction in activity appears to be related to catalyst acidity as can be ascertained from the RAD values in Table I. The most acidic catalyst, i.e. the unpromoted catalyst, possesses the highest hydrodenitrogenation activity; whereas, the least acidic Ca-promoted catalyst exhibits the lowest activity. The Mg-promoted catalyst lies in between these extremes with regard to both acid site density and hydrodenitrogenation activity. It appears that acid sites are essential for good hydrodenitrogenation activity presumably because they provide preferential adsorption sites for basic nitrogen species. Acid sites are evidently not essential for good hydrogenation activity, however.

Properties of the used THF extracted catalysts are compiled in Table IV. By comparison with the fresh catalyst values of Table I, it is apparent that a modest reduction in surface area has occurred with the greatest reduction being for the untreated catalyst. The loss in pore volume is more substantial with the pore volume reduction ranging from 33% for the Ca-promoted catalyst to 49% for the unpromoted catalyst. This is also evident from a comparison of cumulative pore size distributions plotted in Figures 3 and 4.

The most interesting information in Table IV is the carbon deposition data. Indeed promotion with alkaline earth metals does serve to reduce coke deposition. Calcium promotion is more effective than magnesium promotion, and again the results suggest that coke deposition may be related to catalyst acidity.

Higher coke levels are observed on the more acidic catalysts.

The results of this study are broadly consistent with recent results reported by Shimada and coworkers (12). These investigators also observed that doping with Ca and Mg served to reduce both coke level and hydrodenitrogenation activity. Consistent with previous results for sodium promoted catalysts (13) they find that activity losses are reduced by adding the alkaline earth metal as a last step in the preparation, i.e. after the active metals have been added. Somewhat contrary to our findings is their observation that hydrogenation activity is also reduced by the alkaline earth treatment. However, it may be important to note that this conclusion is based on the hydrogenation of a model compound in a batch reactor. Their results thus reflect initial activity levels. As noted above our initial hydrogenation activity appears to be higher for the unpromoted catalyst, but after a few hours on stream this advantage disappears. Similar results were obtained with sodium promoted catalysts (4).

Our results for both alkali (4) and alkaline earth promoted hydrotreating catalysts have been explained in a rather straightforward manner in terms of catalyst acidity. However, in a study of hydrotreating catalysts prepared on different support materials (14), we report findings that appear somewhat contradictory of the present results. In particular we observe a trend of decreasing coke formation with increasing RAD. This may be due to the fact that characterization of catalyst acidity by TPD of t-butylamine is far from complete. In particular, our analysis provides little or no information regarding the strength (11) or type (Bronsted or Lewis) of acidity. These factors may be expected to affect both coking tendency and activity levels.

CONCLUSIONS

The promotion of an otherwise finished CoMo/Alumina hydrotreating catalyst with percentage quantities of alkaline earth metals offers an effective means of reducing coking tendency while maintaining a high hydrogenation activity. The treatment does have an adverse affect on hydrodenitrogenation activity. Alkali and alkaline earth promotion may therefore be beneficial in applications such as coal liquefaction where the primary function of the catalyst is to hydrogenate and the reaction environment is conducive to coking.

ACKNOWLEDGEMENTS

This work was jointly sponsored by the U.S. Department of Energy (Grant DE-FG22-88PC88942) and the Amoco Oil Company. We are grateful for both the financial support and the helpful consultations provided by these organizations.

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Table I
Fresh Catalyst Properties

	<u>Amocat 1A</u>	<u>Mg-Promoted</u>	<u>Ca-Promoted</u>
BET Surface Area, m ² /g	167	144	135
Pore Volume (> 60 Å dia.), cc/g	0.71	0.69	0.69
Avg. Micropore Diameter, Å	130	125	125
Avg. Macropore Diameter, Å	4500	4500	4500
Relative Acid Density, m ⁻²	0.049	0.036	0

Table II
Feedstock Properties (HC01-R)

wt% C	91.43
wt% H	6.84
wt% S	0.20
wt% N	0.68
wt% O (BD)	0.85
wt% Asphaltene	12
wt% Preasphaltene	4
Sp. Gr. (60/60 F)	1.1232

Table III
Nominal Deactivation Run Conditions

Pressure =	2000 psig
Temperature =	440°C (825°F)
WHSV =	3.0
H ₂ Treat Rate =	5500 SCF/BBL

Table IV
Used Catalyst Properties

	<u>Amocat 1A</u>	<u>Mg-Promoted</u>	<u>Ca-Promoted</u>
BET Surface Area, m ² /g	137	137	118
Pore Volume (> 60 Å dia.), cc/g	0.36	0.41	0.46
Avg. Micropore Diameter, Å	100	100	100
Avg. Macropore Diameter, Å	4000	4100	4100
Relative Acid Density, m ⁻²	0.020	0.014	0
Wt% Carbon	17.2	13.2	9.80
Wt% Hydrogen	1.34	1.01	1.03

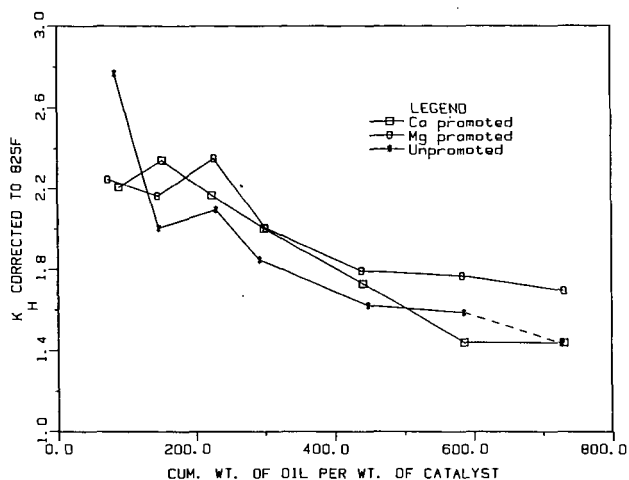


Figure 1. Deactivation curves for hydrogen uptake.

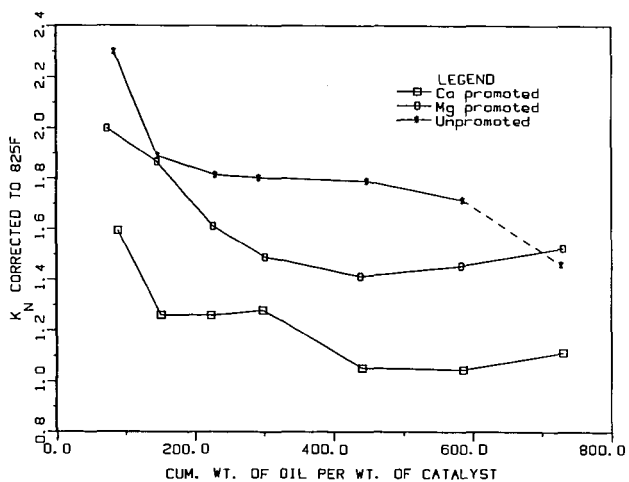


Figure 2. Deactivation curves for hydrodenitrogenation.

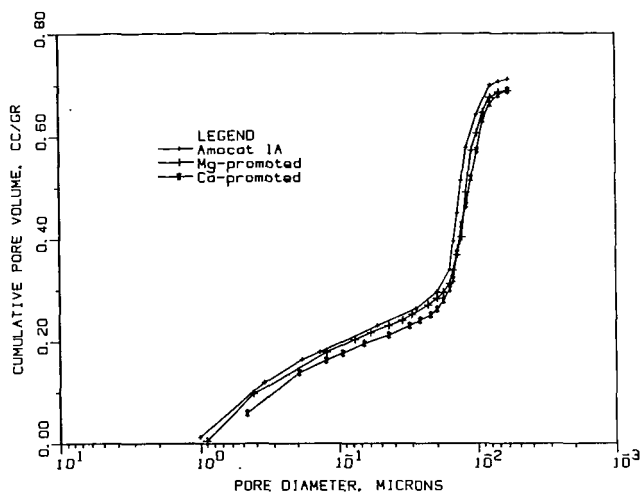


Figure 3. Cumulative pore size distributions for fresh catalysts.

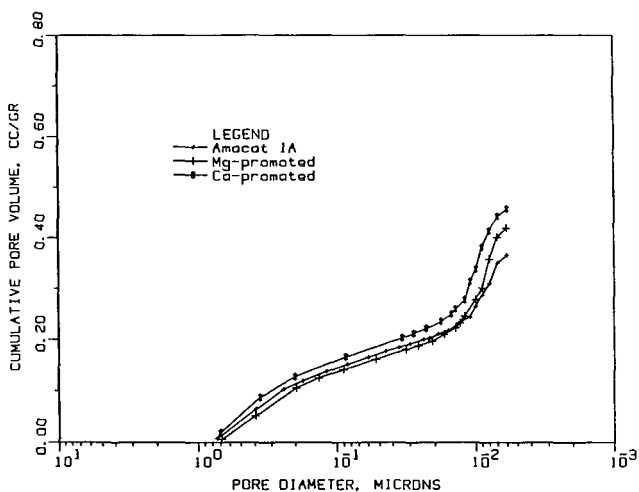


Figure 4. Cumulative pore size distributions for used catalysts.